The experiment and numerical investigations on hydrogen production from ammonia cracking: a priori study

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Abstract

The characteristics of ammonia cracking using Ru/Al_2O_3 catalyst to produce hydrogen are experimentally and numerically investigated by varying temperature of the furnace (450-600ºC). The experimental results show that more than 90% of ammonia is converted into hydrogen if the temperature of the catalytic reactor is above 490ºC (furnace temperature is 550ºC). The successful implementation of the Takahashi's chemical kinetic model [1,2] in Arrhenius form is a crucial step in making the model to be applicable in different numerical frameworks using CHEMKIN format (e.g., ANSYS Fluent [3], OpenFOAM [4] etc.,). In addition, a good agreement in the ammonia conversion rate between experiments and simulations for the Ru/Al_2O_3 catalyst in this study implies that the Ru-based Takahashi's chemical kinetic model can be a good option for the simulations of ammonia decomposition using Ru/Al_2O_3 catalyst in the context of lacking a chemical mechanism.

1 Introduction

Recently hydrogen (H_2) has emerged as an effective and clean alternative to fossil fuels, especially in the power generation sector, to meet carbon neutrality by 2050. Hydrogen production from various sources has been extensively investigated over the past decades due to its high energy capacity and environmental friendliness [5]. One of the challenges in H_2 technologies is its storage and transport since it has a very low energy density by volume. To solve the problem, ammonia (NH_3) that has high hydrogen content and can be easily stored and transported is a good candidate as H_2 carrier for achieving the hydrogen economy in the future [2].

NH_3 decomposition to produce H_2 can be regarded as the reverse process of NH_3 synthesis. It is an endothermic process and often requires high operating temperature to produce very high purity hydrogen. Usually, the required reaction temperature can be reduced significantly via utilization of catalysts [6,7]. Typical catalysts commonly used for NH_3 decomposition include iron (Fe), molybdenum (Mo), ruthenium (Ru), and nickel (Ni), among which Ru-based catalysts have the highest activities [8-10].

Ru-based catalysts have been studied experimentally and numerically by many research groups [1,2,6-11]. However, it is still challenging to numerically investigate since the performance of catalytic NH_3 decomposition depends on many factors including kinetic models, operating pressure and temperature conditions, configurations of reactor, and catalyst preparation etc., especially in the industrial scale. In this sense, our long-term goals are to evaluate the performance of NH_3 decomposition to find the best operating conditions as well as configurations of the catalytic cracker for industrial use with an NH_3 conversion rate as high as possible. This work is considered as one of our priori studies of NH_3 decomposition at the lab-scale using Ru/Al_2O_3 catalyst aiming to find a suitable chemical kinetic model for computational investigation using OpenFOAM [4] framework in the future at industrial scale level.

2 Experiments

2.1 Configuration

Figure 1 illustrates the experimental test rig including a fixed packed-bed catalytic reactor made by 316 stainless steel (18% Cr, 12% Ni, 2% Mo, and balanced Fe) of total length of 500 mm and radius of 5 mm. Ru/Al_2O_3 catalyst particles of diameter of 1 mm are packed inside the reactor of a layer of 97 mm. The reactor is heated externally using an electrical heater (i.e., furnace). Temperatures of preheated zone and inside catalytic reactor are measured by three thermocouples (TC#1-TC#3) while temperature of the furnace is controlled by two other sensors (TC#1 furnace, TC#2 furnace). To keep the pressure in the circuit at the desired value, a back pressure regulator is utilized at the reactor outlet. The outgoing gas, mainly composed of H_2, N_2 and un-reacted NH_3, feeds an air-cooled heat exchanger. The composition of effluent gases was analyzed with on-lined gas chromatograph (GC), and mass spectrometer (MS), and double-checked by comparing two results from both devices. The details of the configuration can be found in Fig. 1 while Fig. 2 shows the real catalytic reactor.

2.2 Catalyst preparation

Alumina (Al_2O_3) beads with 1 mm size were used as a support. ruthenium (Ru) was incorporated onto the alumina support by wet impregnation using Ru precursor solution. The target Ru loading was 3.0 wt%. Before the ammonia decomposition experiments, the catalysts were reduced *in situ* with H_2 at 600ºC for 1 h.

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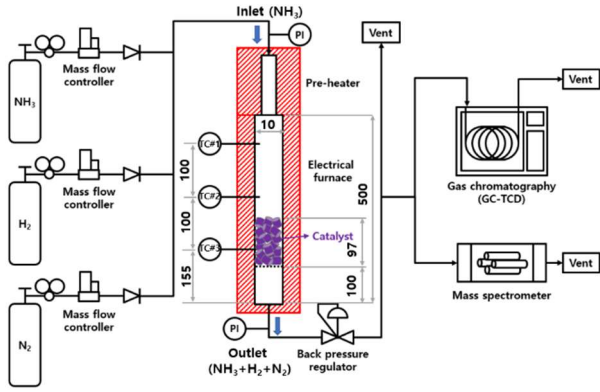E-mail address: csyoo@unist.ac.kr

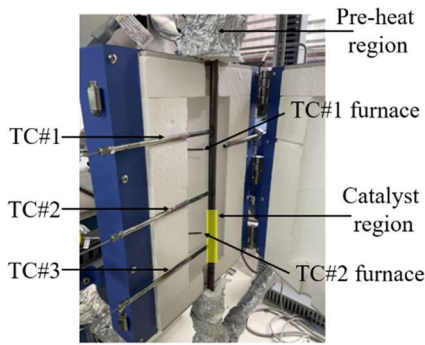Figure 1: Schematic of the experimental setup (dimension in millimeter)

Figure 2: Real catalytic reactor.

2.3 Experiment results

Several experiments are conducted with different temperatures of reactor (from 400-550°C) using the test rig presented above to estimate the performance of NH_3 decomposition under lab-scale conditions. Pure ammonia gas is fed with a gas hourly space velocity (GHSV) of 10,000 mL/g_{cat}.h for all experiments. The results of the performance of catalytic NH_3 decomposition at different temperatures of the reactor using the prepared Ru/Al_2O_3 catalyst (Ru 3 wt%) are shown in Table 1. It can be observed that the catalytic reactor needs to be heated at relatively high temperature (i.e., more than 400°C) to make sure at least 50% of NH_3 can be decomposed. Particularly, at reactor temperature of 407°C only 46.9 % NH_3 is converted into H_2 while it becomes significantly improved when the temperature of reactor is increased by 40°C. Moreover, the 90% conversion rate can be achieved when the reactor is maintained at 491°C. High purity hydrogen product (99% of conversion) is reached when the reactor is heated at 554°C.

The data of furnace temperatures presented in the second column of the Table 1 evidently indicates that the NH_3 decomposition process is highly endothermic such that the furnace always needs to be maintained at least 45-50°C higher than desired value of the catalytic reactor. The first column of the Table 1 shows the values of pre-heat zone in different experiments which are later being used to set the inlet condition for numerical simulations.

Table 1: Effect of reaction temperature on NH_3 conversion over Ru/Al_2O_3 catalyst.

Pre-heat temp. TC#1 (°C)	Furnace temp. (°C)	Reactor temp. (°C)	Conversion rate (%)		
			by GC	by MS	Aver.
365	450	407	48.54	45.27	46.90
410	500	445	69.33	69.44	69.39
453	550	491	90.12	92.45	91.29
492	600	554	97.05	99.77	98.41

temp.: Temperature; by GC: measured by Gas chromatography; by MC: measured by Mass spectrometer; Aver.: averaged value.

3 Numerical calculations

3.1 Numerical framework and modeling

To achieve the better understanding of ammonia cracking process and to support the next phase of the project for industrial scale design, we perform numerical simulations of two-dimensional (2-D) axisymmetric packed-bed catalytic reactor as shown in Fig. 3. The computational domain is a circular tube of total length of $L = 355$ [mm] and radius $R = 5$ [mm], consisting of 10,500 structured elements such that it has 15 points in the radial direction. With this grid size, numerical solutions have been achieved as grid independence. Since the number of cells is relatively small (i.e., less than 500,000), the free ANSYS Fluent 2022R1 platform [3] is employed in this work. For the next phase of this project, OpenFOAM [4] is going to be used for industrial-scale investigations.
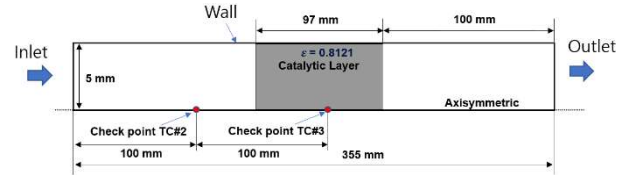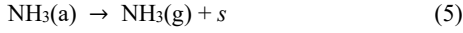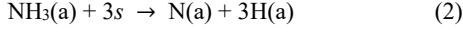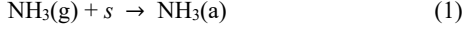

Figure 3: The computational domain.

There are several assumptions have been adopted to simulate the performance of ammonia decomposition in this work such as: (i) all simulations are conducted under steady state conditions; (ii) catalytic particles are isothermal and uniformly spherical of diameter $d_p = 1$ [mm]; (iii) catalytic bed is a continuous phase with homogeneous porosity $\varepsilon = 0.8121$ [-]; (iv) the temperature of fluid and solid at any given point within reactor are uniform; (v) the ideal gas law is applied for gaseous mixture.

The chemical kinetic mechanism is one of the central issues in the computational simulations of catalytic reactions. However, it is difficult to find a chemical mechanism developed for the same components of catalyst. For instance, to the best of the authors' knowledge, there is no detailed chemical kinetic model for ammonia decomposition using the Ru/Al_2O_3 (wt3%) catalyst. To overcome this problem, we first adopted a Ru-based detailed chemical mechanism for NH_3 decomposition developed by Takahashi et al (2016) [1] (referred as Takahashi's model) for the simulations in the present study. Surprisingly, Takahashi's model does very well for Ru/Al_2O_3 catalyst cases although it is originally developed for Ru/MgO catalyst. This will be further discussed in Section 4.

It is essential to change the expressions of rates of surface reactions in Takahashi's model to the Arrhenius form (referred

as modified chemical mechanism) to make it to be applicable in frameworks that adopt CHEMKIN format for chemical mechanism input file such as ANSYS Fluent or OpenFOAM. The detail surface reaction mechanism is rewritten such that it includes six forward elementary reactions since only forward surface reaction is applicable in ANSYS Fluent as follows:

$$NH_3(g) + s \rightarrow NH_3(a) \tag{1}$$

$$NH_3(a) + 3s \rightarrow N(a) + 3H(a) \tag{2}$$

$$2N(a) \rightarrow N_2(g) + 2s \tag{3}$$

$$2H(a) \rightarrow H_2(g) + 2s \tag{4}$$

$$NH_3(a) \rightarrow NH_3(g) + s \tag{5}$$

$$H_2(g) + 2s \rightarrow 2H(a) \tag{6}$$

where s is a vacant site. (g) and (a) denote for a gaseous species and an adsorbed species on the catalyst surface, respectively. The rates of reactions r_i $(i = 1 - 6)$ are expressed in CHEMKIN format with reaction rate constant coefficients are presented in Table 2. It is important to note that values of these coefficients are different from those in the original Takahashi's model since their dimensions are converted to be compatible with CHEMKIN format.

Table 2: The coefficients in reaction rate constant in CHEMKIN format for Ru/Al$_2$O$_3$ catalyst.

Rate constant [mol/m^2-s]	A[-]	β[-]	E_a [kJ/mol]
k_1	1.1479E+10	0	0
k_2	4.7625E+37	0	105.8
k_3	1.1802E+17	0	123.5
k_4	1.3536E+14	0	67.8
k_5	3.2890E+19	0	64
k_6	8.9642E+12	0	0

Heat transfer models also play an important role in ammonia decomposition simulations due to highly endothermic reactions [2] and the heat transfer in porous media is considerably different from conventional purely gas or solid phase simulations [12]. Particularly, a model for wall heat transfer coefficient, h_w[W/m^2-K], in the porous media in this work is [2,12]:

$$\frac{h_w d_p}{\lambda_g} = 3.0 + 0.054 \times RePr \tag{7}$$

where λ_g is the fluid thermal conductivity [W/m-K]. $Re = (d_p \times G)/\mu$, and $Pr = (C_p \times \mu)/\lambda_g$, where G, μ, C_p are fluid superficial mass velocity [kg/m^2-s], the fluid viscosity [kg/m-s], and fluid specific heat capacity [J/kg-K], respectively.

A model for effective thermal conductivity, λ_{eff} [W/m-K] in the porous media in this work is [2,12]:

$$\frac{\lambda_{eff}}{\lambda_g} = \frac{\lambda_{eff}^o}{\lambda_g} + \alpha\beta \times RePr \tag{10}$$

where $\alpha\beta = 0.11$. λ_{eff}^o is effective thermal conductivity with motionless fluid, $\lambda_{eff}^o/\lambda_g = (1 - \varepsilon)/(\lambda_g/\lambda_s + \varphi)$, where λ_s is solid thermal conductivity. The details of these models can be found in [12].

It is of importance to note that the above heat transfer models and the models of surface reaction rates in the modified chemical mechanism are not available in ANSYS Fluent 2022R1. Therefore, user-defined functions (UDFs) are adopted to implement the models in the present study. The validations of their implementations are presented in Section 3.2.

3.2 Validation of UDFs implementation

To validate the implemented UDFs, we perform 2-D simulations of an axisymmetric packed bed catalytic reactor under scaled-up conditions (SV=15000 h^{-1}, V=10m^3/h) with different inlet gas temperature and different inner wall temperature. The detailed configurations and boundary conditions can be found in [2]. The simulation results are then compared to the benchmark data from Takahashi et al. [2] as presented in Fig. 4 and Fig. 5. It can be seen from these figures that in general, the results obtained from the present study are in considerably good agreement with benchmark data, implying the implementation of models in UDFs are proper. Particularly, the NH$_3$ conversion rates obtained from our simulations are almost identical to that of achieved by Takahashi and coworkers [2] for the different inlet temperature cases (see Fig. 4) while for the cases with different inner wall temperature the rates of NH$_3$ conversion showed a slightly underestimated. This is understandable because the framework used in the present work is not totally the same as the one used in the work of Takahashi et al. For instance, the molecular diffusivity model in [2] is based on Wilke's mixed law in a multicomponent system while the present work adopted Kinetic theory model.
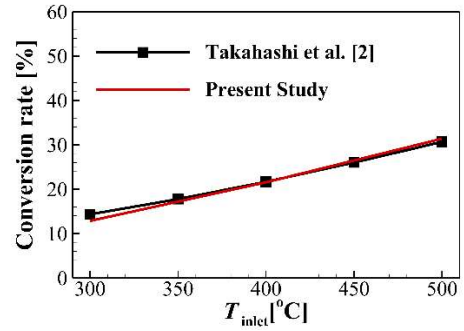

Figure 4: Validation of UDFs implementation for different inlet temperature. The black line is benchmark data taken from [2]. The red line is data obtained in the present study.
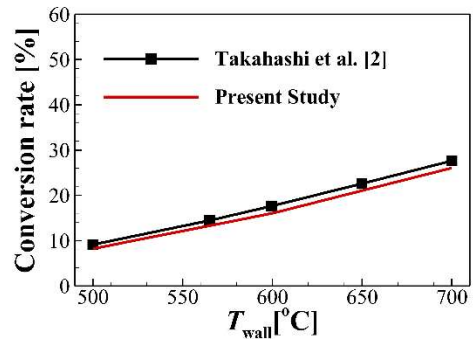

Figure 5: Validation of UDFs implementation for different inner wall temperature. The black line is benchmark data taken from [2]. The red line is data obtained in the present study.

3.3 Simulation results

Using the models above, we simulate 2-D axisymmetric catalytic reactor of NH$_3$ decomposition using Ru/Al$_2$O$_3$ catalyst. Boundary conditions for velocity at the inlet in all simulations are set to those of the experiments such that GHSV is equal to

10,000 mL/g_{cat}h. Inlet temperature is set to the value of TC#1 as in the experiments (see the first column of the Table 1). Constant wall temperature boundary conditions are applied to the heated wall of the computational domain such that temperatures inside the reactor are identical with the recorded temperature in experiments (see the second column of the table 1). For the kinetic model, conceptually, we need to use a a chemical mechanism that originally developed for NH_3 decomposition using Ru/Al_2O_3 catalysts. However, Ru-based chemical kinetics taken from Takahashi et al. [2] is used since currently there is no such kind of chemical kinetics for exact components of that catalyst.

Figure 6 illustrates the conversion rate of NH_3 at different furnace temperatures ranging from 450 to 600°C. It can be observed that data obtained by computational simulations are in reasonably good agreement with experiments. However, at lower temperature conditions the simulated results are underestimated compared to experiments while overestimation in NH_3 conversion rate is observed when temperatures of furnace are increased. The conversion predicted by simulations reaches 100% as the temperature of furnace is 550°C while experimentally it is approximately 92%. We conjecture that the deviations between the experiments and simulations would largely originate from the chemical mechanism.
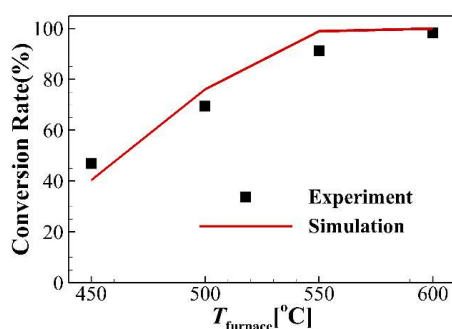

Figure 6: Comparison in ammonia conversion rate between simulation and experiments under different furnace temperature conditions. The symbols are experimental data (averaged values). Line represents conversion rates predicted by numerical simulations.

4 Discussions

The numerical investigations of NH_3 decomposition are still challenging because of the limitation of available detailed kinetic models for chemical surface reactions occurring in catalytic processes. In this work, we found that the coefficients of the reaction rate constants of Takahashi's surface chemical mechanism [1] which was originally developed for Ru/MgO catalyst can be used for numerical simulations of Ru/Al_2O_3 catalyst with acceptable accuracy.

For such kind of experiments as same as in the present work, using the temperature of the furnace as the constant wall temperature boundary condition in the computational investigations is not always true since NH_3 decomposition is highly endothermic. More investigations in heat transfer are needed to be able to reflect the actual process of the catalytic NH_3 decomposition.

5 Conclusions

The ammonia decomposition to produce hydrogen using the Ru/Al_2O_3 catalyst was investigated by means of experiments combining computational fluid dynamics under lab-scale conditions with different temperatures of the furnace (450-600°C). The experimental results show that more than 90 % of ammonia is converted into hydrogen if the temperature of the catalytic reactor achieves 490°C (furnace temperature is 550°C). The numerical simulations successfully reproducing the work of Takahashi et al. [1, 2] by utilizing a modified Ru-based catalyst chemical mechanism which can be implemented easily in frameworks using CHEMKIN format (e.g., ANSYS Fluent [3], OpenFOAM [4] etc.,) confirms that transformations of surface reaction rates in Takahashi's form into Arrhenius form are proper. In addition, a good agreement in the ammonia conversion rate between experiments and simulations for the Ru/Al_2O_3 catalyst in the present study implies that the Ru-based Takahashi's chemical kinetic model might be a good option for simulations of ammonia decomposition using Ru/Al_2O_3 catalyst in the context of lacking a detailed chemical model.

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